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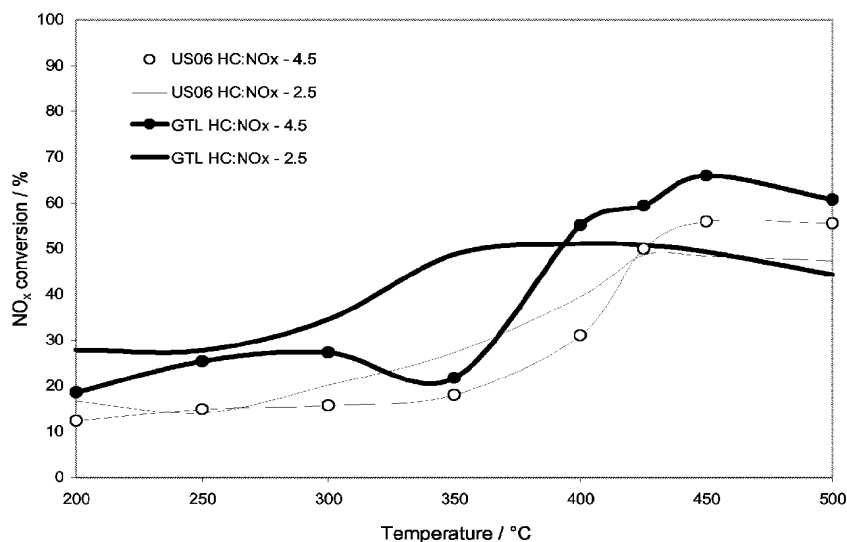
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[Continued on next page]

(54) **Title:** REDUCING COKING OVER AG/AL₂O₃ HC-SCR CATALYST



(57) **Abstract:** The present invention relates to a method of reducing coking over a AgZAl₂O₃ hydrocarbon selective catalytic reduction catalyst in an exhaust stream of a lean burn internal combustion engine, the exhaust stream comprising hydrocarbon and NO_x. The method comprises controlling the hydrocarbon to molar NO_x ratio of the exhaust stream so as to be within certain limits at certain temperatures. An exhaust system for a lean burn engine suited to the above method, and a lean burn internal combustion engine, or a vehicle or stationary power source comprising such an exhaust system are also disclosed.

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REDUCING COKING OVER Ag/Al₂O₃ HC-SCR CATALYST

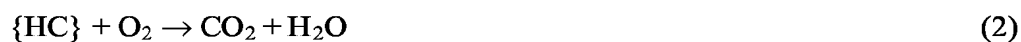
This invention relates to a method of reducing coking of Ag/Al₂O₃ hydrocarbon selective catalytic reduction (HC-SCR) catalysts in a lean burn engine exhaust gas stream.

HC-SCRs are sometimes also referred to in the literature as non-selective catalytic reduction (NSCR) catalysts, lean NO_x catalysts (LNC), lean NO_x reduction catalysts, "DeNO_x catalysts" and NO_x occluding catalysts.

In hydrocarbon selective catalytic reduction, hydrocarbons (HC) react with nitrogen oxides (NO_x), rather than oxygen (O₂), to form nitrogen (N₂), carbon dioxide (CO₂) and water (H₂O) according to Reaction (1):



The competitive, non-selective reaction with oxygen is given by Reaction (2):



The most effective HC-SCR catalysts used to selectively promote the desired reaction (1) are Pt/Al₂O₃, Cu exchanged ZSM-5 and Ag/Al₂O₃. Ag/Al₂O₃ catalysts operate at higher temperatures and over a broad temperature range, and have recently shown promise in vehicle testing (Klingstedt et al., Topics in Catalysis, 30/31, 2004, 27 and Lindfors et al., Topics in Catalysis, 28, 2004, 185, the entire contents of which are incorporated herein by reference).

All of these catalysts exhibit high activity for the selective reduction of NO_x by hydrocarbons, including long chain alkane and diesel fuel, but each type of catalyst suffers from some form of limitation in use. Pt/Al₂O₃ catalysts display lower NO_x conversion and lower selectivity towards nitrogen; N₂O (conversion >60%) is a basic

product. Additionally, the HC-SCR activity window of Pt/Al₂O₃ catalysts is limited to low temperatures (about 150 – 250 °C). Generally speaking, Cu/ZSM-5 catalysts can suffer from thermal deactivation due to copper sintering and dealumination of the zeolite. Ag/Al₂O₃ catalysts are tolerant to hydrothermal ageing, but can suffer from chemical deactivation caused by coking or sulphation. We understand that the relatively poor performance of Pt/Al₂O₃ catalysts and the relatively poor activity of Cu/ZSM-5 and Ag/Al₂O₃ HC-SCR catalysts once aged, has so far been insufficient to allow for their widespread implementation (Konig et al., Topics in Catalysis, 28, 2004, 99, incorporated herein by reference).

Coking is not a significant factor in the activity of any HC-SCR catalyst at higher temperatures since above approximately 400 °C any carbon present will be burnt to form CO₂ thereby leaving the catalyst surface available for reactions to take place thereon. As such it is important to differentiate between the absolute activity of any particular HC-SCR catalyst, and the reduction in activity that coking may result in. An increase in the absolute activity of any particular HC-SCR catalyst will not necessarily be the result of a concomitant reduction in coking.

Nonetheless, coking does have a significant affect upon the HC-SCR activity of Ag/Al₂O₃ catalysts at lower temperatures and therefore we devised a means of limiting access of the hydrocarbon species responsible for coke deposition to the catalyst to minimise coking deactivation. Said means involved modifying the Ag/Al₂O₃ catalyst formulation, and is disclosed in WO 2005/016496 (incorporated herein by reference). Specifically, we disclosed that by combining known HC-SCR catalysts with a partial oxidation catalyst (POC) that it was possible to suppress or avoid low temperature coke formation. In the WO 2005/016496 invention, the POC helps to prevent coking by promoting the partial oxidation of hydrocarbons in the exhaust gas of a lean-burn internal combustion engine to carbon monoxide (CO), hydrogen gas (H₂) and partially oxygenated hydrocarbon species. Therefore the heavy hydrocarbon species present in the exhaust gas are partially oxidised to smaller, more reactive species prior to contacting the downstream HC-SCR catalyst.

We have now discovered a new method for reducing coking over a Ag/Al₂O₃ HC-SCR catalyst without needing to modify catalyst formation by optimising the hydrocarbon to molar NO_x ratio (HC:NO_x as C1) of the exhaust gas to achieve high NO_x conversion for Ag/Al₂O₃ HC-SCR catalysts across a wide temperature range.

5

According to a first aspect, the invention provides a method of reducing coking over a Ag/Al₂O₃ hydrocarbon selective catalytic reduction (HC-SCR) catalyst in an exhaust stream of a lean burn internal combustion engine, which exhaust stream comprising hydrocarbon and NO_x, which method comprising controlling the hydrocarbon to molar NO_x ratio of the exhaust stream so as to be less than or equal to 2.0 when the exhaust stream temperature is less than or equal to 300 °C, between 2.0 and 4.5 when the exhaust stream temperature is from 300 °C to 425 °C, and 4.5 or greater when the exhaust stream temperature is greater than or equal to 425 °C. The temperature of the exhaust stream relevant to this invention is the temperature of the exhaust stream as it impacts the HC-SCR catalyst.

15

In the course of our research we discovered that the selective catalytic reduction of NO_x using hydrocarbons by Ag/Al₂O₃ catalysts varies depending upon the hydrocarbon used (see Figure 1). Short chain alkanes, e.g. octane and decane, show poor NO_x conversion whilst long chain alkanes show good initial activity although this decreases with time due to coking, as explained above.

20

This connection between the hydrocarbon being used in the selective catalytic reduction of NO_x and activity of Ag/Al₂O₃ catalysts led us to investigate how, in addition to varying the HC:NO_x ratio in response to temperature, we might vary the HC:NO_x ratio depending upon the hydrocarbon being used. As a result we found that by varying the HC:NO_x ratio depending upon the aromatics content of the hydrocarbon being used we were able to maintain good high temperature activity and minimise low temperature deactivation through coking. Therefore, in one embodiment the hydrocarbon has a relatively low aromatics species content, e.g. comprising from 0 to 10% aromatics. When this method is applied to hydrocarbon with a relatively low aromatics species content, the HC:NO_x is controlled so as to be between 0.5 and 2.0 when the exhaust gas temperature is less than or equal to 300 °C

30

and between 4.5 and 7.0 when the exhaust gas temperature is greater than or equal to 425 °C. In an alternative embodiment the hydrocarbon species has a relatively high aromatics species content, e.g. comprising from 10 to 40% aromatics. When this method is applied to hydrocarbon with a relatively high aromatics species content, the

5 HC:NO_x is controlled so as to be between 1.0 and 2.0 when the exhaust gas temperature is less than or equal to 300 °C and between 4.5 and 5.0 when the exhaust gas temperature is greater than or equal to 425 °C.

“Aromatics” as defined herein include, but are not limited to, the following

10 species: toluene, ethylbenzene, xylenes, polaromatics, 1-methylnaphthalene, n-pentylbenzene, biphenyl, 1-butylnaphthalene, n-nonylbenzene, 2-octylnaphthalene and n-tetradecylbenzene.

Controlling the HC:NO_x ratio of the exhaust stream can be achieved by either

15 varying the amount of hydrocarbon present in response to the amount of NO_x present, or by varying the amount of NO_x present in response to the amount of hydrocarbon present. This can be achieved by monitoring the levels of NO_x or hydrocarbon present in the exhaust stream, or predicting the levels of NO_x or hydrocarbon present in the exhaust stream. Such levels may be predicted by referring to the NO_x or

20 hydrocarbon levels known to be present during certain engine conditions.

The hydrocarbon for use in the present invention may be injected into the engine exhaust stream upstream of the HC-SCR catalyst, or it may be produced by cracking engine fuel. Engine fuel may be cracked in the cylinder of the engine or in

25 the exhaust gas stream. For further details of ways to crack engine fuel see patent application no. PCT/GB2006/002595 (incorporated herein by reference).

Exhaust Gas Recirculation or fuel combustion techniques, such as HCCI during a relevant portion of the engine speed/load map, may be used to alter the

30 supply of NO_x to the HC-SCR catalyst.

Suitable engine fuels include those that have relatively high aromatics hydrocarbon species content such as diesel (including US06, an Ultra Low Sulphur

Diesel-ULSD for implementation in 2007) and gasoline, and those that have relatively low aromatics hydrocarbon species content such as FT-GTL (Fischer-Tropsch gas to liquids) and biodiesel.

5 One characteristic of Ag/Al₂O₃ catalysts is the ability of hydrogen to promote its HC-SCR activity. It has been reported in the literature (Satokawa, Chem. Lett., 2000, 294 and Satokawa et. al., Appl. Cat. B, 42, 2003, 179 and Shibata et. al., Phys. Chem., 5, 2003, 2154, the entire contents of which are incorporated herein by reference) that the role of hydrogen is to activate the Ag₂O clusters present on the
10 alumina or to modify the hydrocarbon species (e.g. by oxygenation) to generate more active species for NO_x reduction. In one embodiment of the present invention the exhaust gas stream also comprises hydrogen. We have found that hydrogen can have an advantageous effect on HC-SCR activity at relatively low levels, e.g. less than 1000 ppm, optionally less than or equal to 600 ppm. Whilst it is possible to increase
15 hydrogen content in an exhaust gas by combusting hydrocarbon fuel, e.g. injected into the exhaust gas upstream of the HC-SCR, or by engine calibration, such an increase in hydrogen is generally accompanied by an increase in hydrocarbon as well. In a particular embodiment, relatively low levels of hydrogen can be introduced into the exhaust gas without simultaneously increasing hydrocarbon content of the exhaust gas
20 by contacting a reforming catalyst with hydrocarbon.

 According to a second aspect, this invention provides an exhaust system for a lean burn engine, which system comprising a Ag/Al₂O₃ HC-SCR catalyst and means, when in use, for controlling the HC:NO_x ratio of the exhaust gas so as to be less than
25 or equal to 2.0 when the exhaust stream temperature is less than or equal to 300 °C, between 2.0 and 4.5 when the exhaust stream temperature is from 300 °C to 425 °C, and 4.5 or greater when the exhaust stream temperature is greater than or equal to 425 °C.

30 In practice, the HC:NO_x can be controlled by adjusting the HC concentration in the exhaust gas, by adjusting the NO_x concentration in the exhaust gas, or both. In one embodiment, the exhaust system comprises means, when in use, for controlling the supply of the hydrocarbon. Such means can comprise means for injecting

hydrocarbon into exhaust gas upstream of the HC-SCR catalyst or for adjusting the timing of fuel injection into one or more engine cylinders. In another embodiment, the exhaust system comprises means, when in use, for controlling the supply of NO_x. NO_x control means can comprise Exhaust Gas Recirculation or fuel combustion techniques such as HCCI during a relevant portion of the engine speed/load map. In either of these two embodiments, the control means may include a pre-programmed electronic control unit.

In another embodiment, the exhaust system comprises means for increasing the amount of hydrogen present in the exhaust gas stream. Such means can include a fuel reformer, based on platinum group metals or nickel (see Trimm et al., Catalysis Reviews – Science and Engineering, 43, 2001, 31-84, incorporated herein by reference).

As in the method detailed above, the hydrocarbon species may be injected into the engine exhaust gas stream upstream of the HC-SCR catalyst, or it may be produced by cracking engine fuel, thereby to produce shorter chain hydrocarbons. If the hydrocarbon species is produced by cracking engine fuel, this cracking may be done in the combustion cylinder of the engine or in the exhaust gas stream. Therefore the exhaust system may comprise means for injecting hydrocarbon species into the exhaust gas stream or means for cracking engine fuel in either the combustion cylinder of the engine or in the exhaust gas stream.

According to further aspects, the invention provides a lean burn internal combustion engine including an exhaust system according to the invention, and a vehicle or stationary power source including such a lean burn engine.

In order that the invention may be more fully understood, the following Examples are provided by way of illustration only and with reference to the accompanying drawings, in which:

Figure 1 shows how NO_x conversion activity at 250 °C varies with time for different fuels;

Figure 2 shows how the steady state NO_x conversion activity varies with temperature for both GTL and US06 fuels at hydrocarbon to NO_x ratios of 2.5 and 4.5;

- 5 Figure 3 shows how NO_x conversion activity at 300 °C varies with time for both GTL and US06 fuels at hydrocarbon to NO_x ratios of 2.5 and 4.5;

Figure 4 shows how the steady state NO_x conversion activity varies with temperature for both GTL and US06 fuels at optimised hydrocarbon to NO_x ratios; and

10

Figure 5 shows how the steady state NO_x conversion activity of US06 fuel (at optimised hydrocarbon to NO_x ratios) varies with temperature with either 300 ppm or 600 ppm H₂ present in the gaseous mixture.

- 15 Figure 6 shows how the steady state NO_x conversion activity of US06 fuel (at optimised hydrocarbon to NO_x ratios) varies with temperature with 300 ppm H₂ present in the gaseous mixture at low levels of NO_x.

Example 1

20

Catalyst Formation

2 wt% Ag/Al₂O₃ catalysts were prepared by wet impregnation. Silver nitrate was dissolved in the appropriate amount of water according to the pore volume of the alumina support. The nitrate solution was then added to the support with mixing.

- 25 After drying overnight, the sample was calcined in air at 500 °C for 2 hours.

Example 2

Testing Conditions

- 30 The HC-SCR activity of the catalysts was measured by flowing diesel type fuels (US06 or GTL) in a gaseous mixture (NO 500ppm, hydrocarbon (C1 equivalent) 2250ppm, CO 240ppm, O₂ 12%, H₂O 5%, CO₂ 4.6%, balance N₂ at a total flow rate of 3 L/min) over 0.6 g of catalyst.

NO_x conversions were typically measured after 10 mins at constant catalyst inlet temperature starting from 200 °C and increasing the temperature in 50 °C intervals to 500 °C. We refer to this as steady-state NO_x conversion.

5

Example 3

Effect of Hydrocarbon used on the Reactivity of 2 wt% Ag/Al₂O₃

Figure 1 shows the steady state NO_x concentration for hydrocarbon to NO_x ratio of 4.5 for n-octane, n-decane, n-dodecane, GTL and US06 at 250 °C as a function of time. Octane and decane show poor NO_x conversion whilst dodecane shows good initial activity although its high reactivity, relative to GTL and US06, also promotes coke deposition therefore leading to a rapid decrease in reactivity.

15

Example 4

Effect of HC:NO_x on the Reactivity of 2 wt% Ag/Al₂O₃

The steady state NO_x conversion activity for 2 wt% Ag/Al₂O₃ of Example 1 was measured for hydrocarbon to NO_x ratios of 2.5 and 4.5 using GTL and US06 fuel as the source of the hydrocarbon species.

20

Figure 2 shows that the NO_x conversion activity is generally higher for GTL than for US06 and that NO_x conversion is more effective using the lower HC:NO_x at lower temperatures. The difference in performance between GTL and US06 may be partly due to the higher cetane number of GTL relative to US06, see Table 1. Additionally, we believe the improvement in NO_x conversion is due to deactivation through coking occurring at temperatures of less than 400 °C (the 50% distillation temperature of both fuels is approx. 300 °C, see Table 1) and less hydrocarbon species being present results in less coking. However, at higher temperatures the higher HC:NO_x is more effective for NO_x conversion.

30

| Fuel Analysis | Method | US06 | GTL |
|--|------------|-------------|------------|
| Cetane Number | ASTM D613 | 53.9 | 79 |
| Density at 15 °C (kg m ⁻³) | ASTM D4052 | 827.1 | 784.6 |
| Viscosity at 40 °C (cSt) | ASTM D445 | 2.467 | 3.497 |
| 50% distillation (°C) | ASTM D86 | 264 | 295.2 |
| 90% distillation (°C) | ASTM D86 | 329 | 342.1 |
| LCV (MJ kg ⁻¹) | | 42.7 | 43.9 |
| Sulphur (mg kg ⁻¹) | ASTM D2622 | 46 | 0.05 |
| AROMATICS (wt%) | | 24.4 | 0.3 |
| C (% wt) | | 86.5 | 85 |
| H (% wt) | | 13.5 | 15 |
| O (% wt) | | - | - |
| H/C Ratio (Molar) | | 1.88 | 2.10 |

Table 1. Diesel fuel properties

5 Figure 3 shows the steady state NO_x concentration for hydrocarbon to NO_x ratios of 2.5 and 4.5 for GTL and US06 at 300 °C as a function of time. Although initial NO_x conversion was lower when the HC:NO_x ratio was reduced from 4.5 to 2.5 the rate of catalyst deactivation was also lower at the low HC:NO_x, such that after 30 minutes the NO_x conversion was higher for the HC:NO_x = 2.5 samples.

10

Figure 4 shows the NO_x conversion activity for optimised hydrocarbon to NO_x ratios for US06 and GTL fuels. (By optimised we mean that the HC:NO_x was increased, in accordance with the invention, as the temperature of the exhaust stream increased.) The variable ratios for the two sources of hydrocarbon are also given, see right hand
 15 axis. These results show that optimisation of HC:NO_x improves the HC-SCR activity across the whole temperature window.

Example 5**Effect of Hydrogen on the Reactivity of 2 wt% Ag/Al₂O₃**

- 5 The steady state NO_x conversion activity for 2 wt% Ag/Al₂O₃ of Example 1 with either 300 ppm or 600 ppm H₂ present in the gaseous mixture was measured for optimised hydrocarbon to NO_x ratios using US06 fuel as the source of the hydrocarbon species.
- 10 Figure 5 shows significant improvements in the HC-SCR catalyst activity results from the addition of H₂ with the activity window broadening towards lower temperatures, even at low levels of H₂ addition.

Similar results were obtained using GTL fuel as the source of the hydrocarbon species.

15

Example 6**Effect of NO_x levels on the Reactivity of 2 wt% Ag/Al₂O₃**

- 20 The 300 ppm H₂ test from Example 5 was repeated using a gas mixture containing 200 ppm NO_x, and with the amount of US06 present adjusted to maintain optimised hydrocarbon to NO_x ratios.

Figure 6 shows that the HC-SCR catalyst is highly effective at low levels of NO_x, as well as at higher levels of NO_x.

25

CLAIMS:

1. A method of reducing coking over a Ag/Al₂O₃ hydrocarbon selective catalytic reduction (HC-SCR) catalyst in an exhaust stream of a lean burn internal combustion engine, which exhaust stream comprising hydrocarbon and NO_x, which method comprising controlling the hydrocarbon to molar NO_x ratio (HC:NO_x) of the exhaust stream so as to be less than or equal to 2.0 when the exhaust stream temperature is less than or equal to 300 °C, between 2.0 and 4.5 when the exhaust stream temperature is from 300 °C to 425 °C, and 4.5 or greater when the exhaust stream temperature is greater than or equal to 425 °C.
2. A method according to claim 1, wherein the hydrocarbon comprises from 0 to 10% aromatics species.
3. A method according to claim 2, wherein the HC:NO_x is controlled so as to be between 0.5 and 2.0 when the exhaust stream temperature is less than or equal to 300 °C and between 4.5 and 7.0 when the exhaust stream temperature is greater than or equal to 425 °C.
4. A method according to claim 1, wherein the hydrocarbon comprises from 10 to 40% aromatics species.
5. A method according to claim 4, wherein the HC:NO_x is controlled so as to be between 1.0 and 2.0 when the exhaust stream temperature is less than or equal to 300 °C and between 4.5 and 5.0 when the exhaust stream temperature is greater than or equal to 425 °C.
6. A method according to any preceding claim, comprising the step of monitoring the amount of NO_x present in the exhaust stream and altering the amount of hydrocarbon present in the exhaust stream in response thereto.

7. A method according to any of claims 1 to 5, comprising the step of predicting the amount of NO_x present in the exhaust stream based on engine performance and altering the amount of hydrocarbon present in the exhaust stream in response thereto.
- 5 8. A method according to any of claims 1 to 7, comprising the step of monitoring the amount of hydrocarbon present in the exhaust stream and altering the amount of NO_x present in the exhaust stream in response thereto.
9. A method according to any of claims 1 to 7, comprising the step of predicting
10 the amount of hydrocarbon present in the exhaust stream based on engine performance and altering the amount of NO_x present in the exhaust stream in response thereto
10. A method according to any preceding claim, wherein the hydrocarbon is
15 injected into the engine exhaust stream upstream of the HC-SCR catalyst.
11. A method according to any preceding claim, wherein the hydrocarbon species is produced by cracking engine fuel in either the combustion cylinder of the engine or in the exhaust stream.
- 20 12. A method according to any preceding claim, wherein the exhaust stream also comprises hydrogen.
13. A method according to claim 12, wherein the hydrogen is present at less than
25 1000 ppm, optionally less than or equal to 600 ppm.
14. An exhaust system for a lean burn internal combustion engine, which system comprising a Ag/Al₂O₃ HC-SCR catalyst and means, when in use, for controlling the HC:NO_x ratio of the exhaust stream so as to be less than or equal to 2.0 when the
30 exhaust stream temperature is less than or equal to 300 °C, between 2.0 and 4.5 when the exhaust stream temperature is from 300 °C to 425 °C, and 4.5 or greater when the exhaust stream temperature is greater than or equal to 425 °C.

15. An exhaust system according to claim 14, comprising means, when in use, for controlling the supply of the hydrocarbon.
16. An exhaust system according to claim 15, wherein the means for controlling
5 the supply of the hydrocarbon comprises means for injecting hydrocarbon species into the exhaust stream.
17. An exhaust system according to claim 15, wherein the means for controlling
10 the supply of the hydrocarbon comprises means for adjusting the timing of fuel injection into one or more engine cylinder.
18. An exhaust system according to any of claims 14 to 17, comprising means, when in use, for controlling the supply of NO_x.
- 15 19. An exhaust system according to claim 18, wherein the means for controlling the supply of NO_x comprises Exhaust Gas Recirculation
20. An exhaust system according to claim 18, wherein the means for controlling the supply of NO_x comprises a fuel combustion technique, e.g. HCCI
20
21. An exhaust system according to any of claims 14 to 20, wherein the control means includes a pre-programmed electronic control unit.
22. An exhaust system according to any of claims 14 to 21, comprising means for
25 increasing the amount of hydrogen present in the exhaust stream.
23. An exhaust system according to claim 22, comprising means for cracking engine fuel in the exhaust stream upstream of the HC-SCR catalyst.
- 30 24. An exhaust system according to claim 22, comprising means for cracking engine fuel in the cylinder of the engine.

25. An exhaust system according to claim 22, comprising means for introducing hydrogen into the exhaust stream without simultaneously increasing hydrocarbon content of the exhaust stream by contacting a hydrocarbon with a reforming catalyst.
- 5 26. A lean burn internal combustion engine including an exhaust system according to any of claims 14 to 25.
27. A vehicle or stationary power source including a lean burn engine according to claim 26.

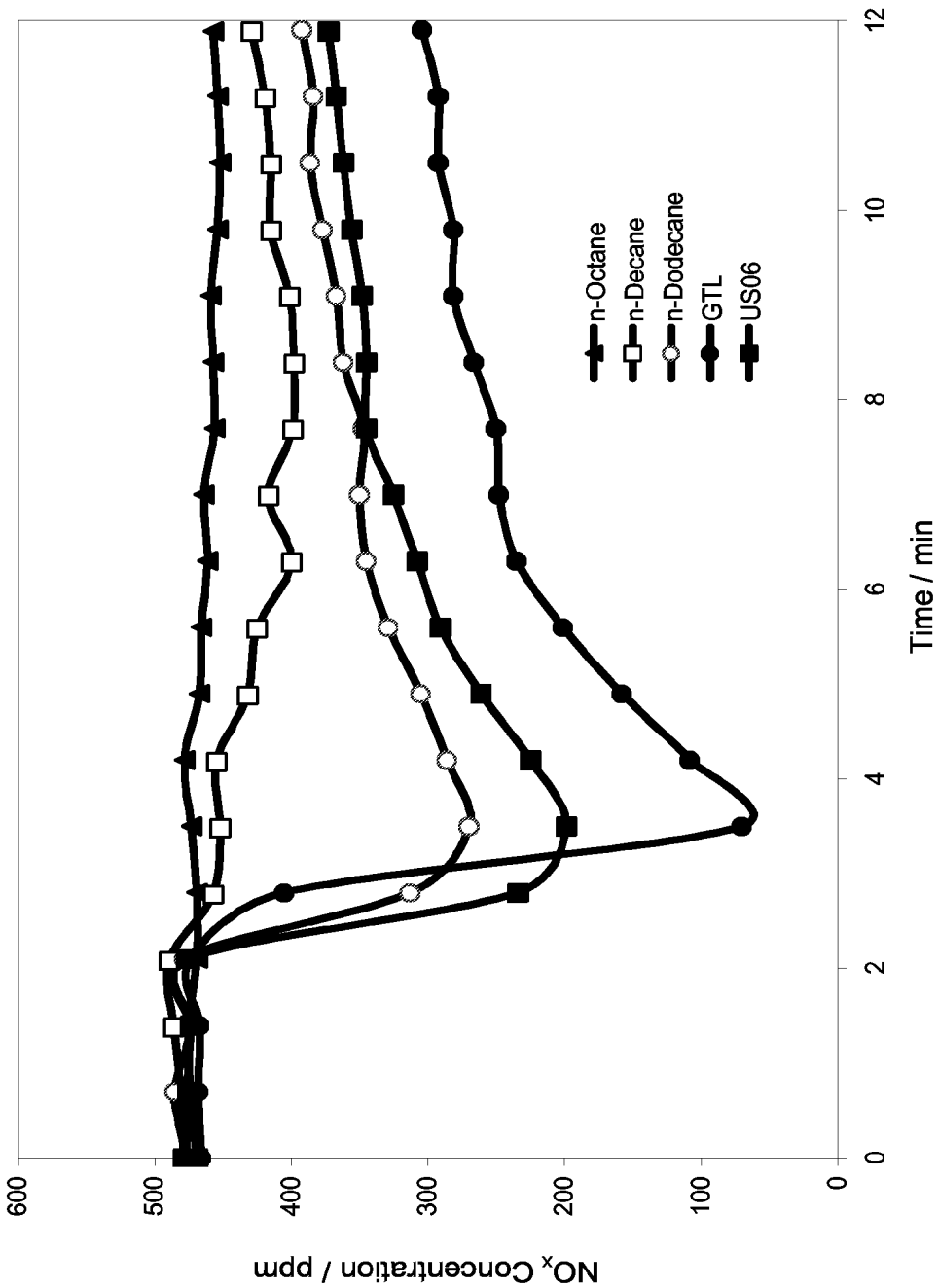


Figure 1

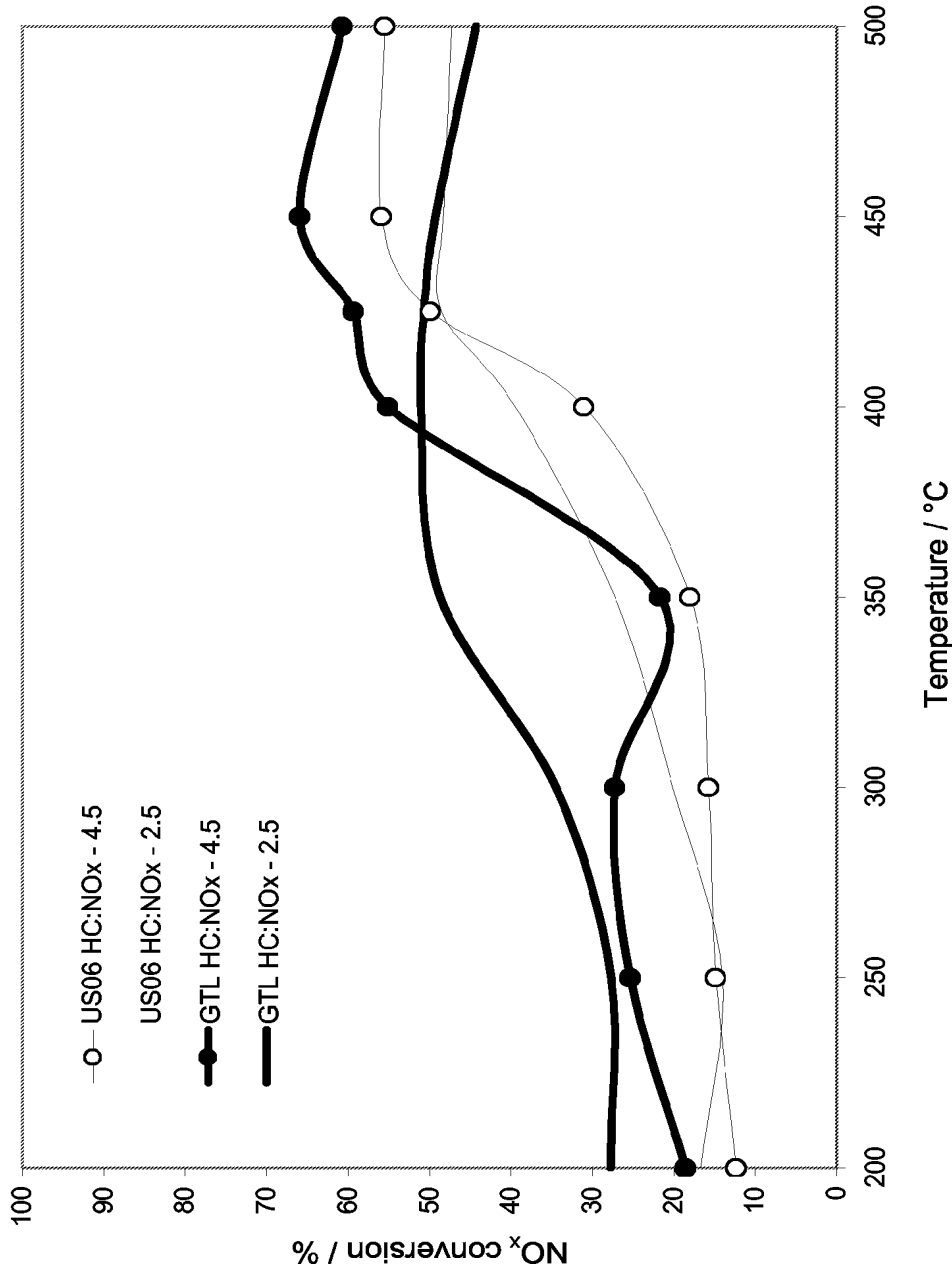


Figure 2

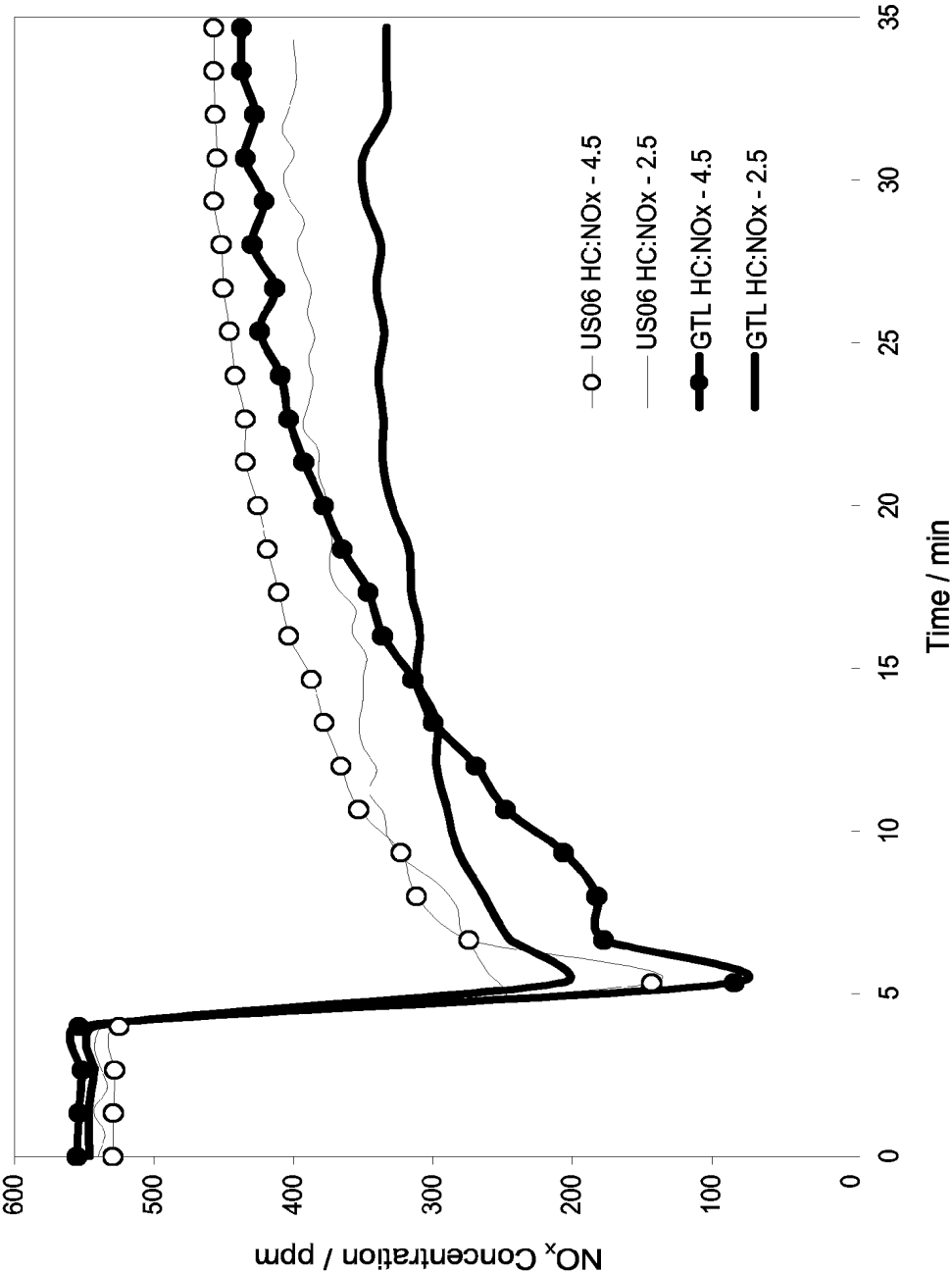


Figure 3

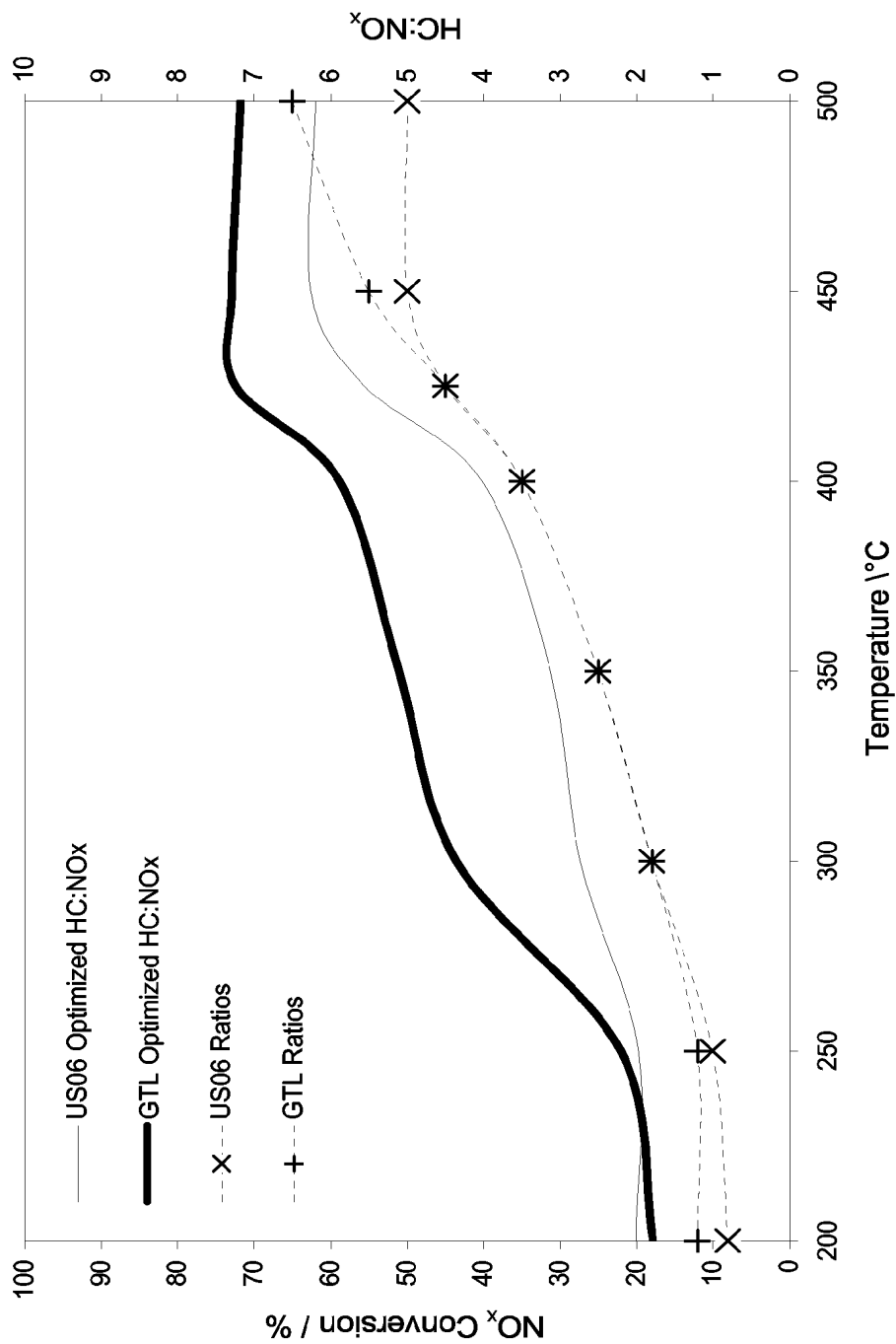


Figure 4

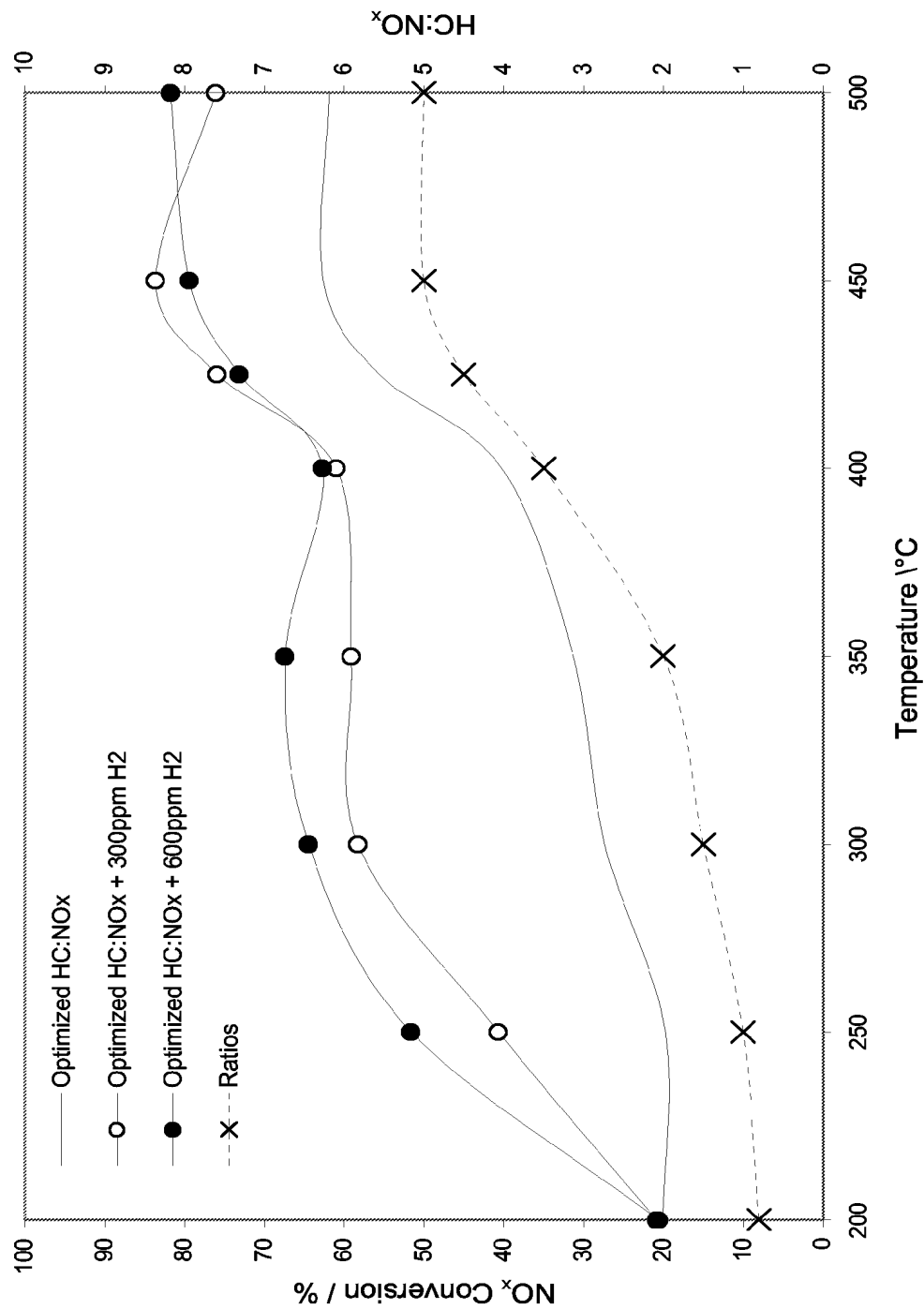


Figure 5

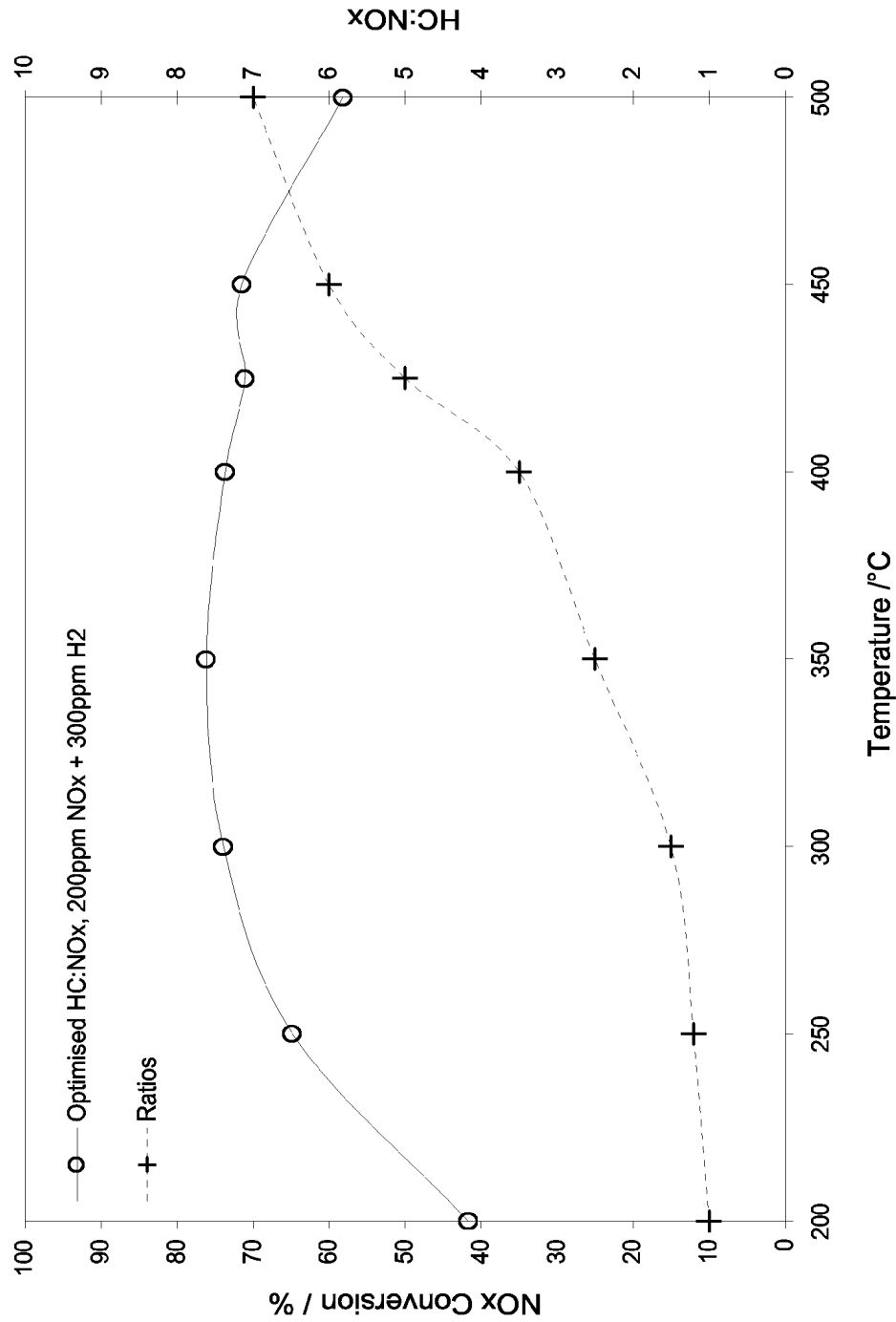


Figure 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/050376

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/90 B01D53/94 F01N3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | US 5 534 237 A (YOSHIDA KIYOHIDE [JP] ET AL) 9 July 1996 (1996-07-09) | 14-18, 26,27 22 |
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| A | US 6 199 372 B1 (WAKAMOTO KOUTARO [JP]) 13 March 2001 (2001-03-13) the whole document | 1-27 |

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☒ See patent family annex.

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